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RAPID COMMUNICATION

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Normal two-electron systems with exponential correlation

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Abstract : Correlated wavefunctions are reported for the ground state of helium isoelectronic systems in the standard form . $\Psi = \phi(r_1)\phi(r_2)\chi(r_{12}) = \sum c_i r_1^{l_i} r_2^{m_i} r_{12}^{n_i} \exp[-(Ar_1 + Br_2 + \mu_i r_{12})] + (1 \rightleftharpoons 2)$, where $l_i + m_i + n_i \leq \omega$ (integer) The set of exponential correlation parameter μ_i is optimised by the Monte Carlo method alongwith other nonlinear variational parameters A, B to obtain quite accurate eigenenergies. The best wavefunction for helium with only 25 terms in the present scheme predicts an eigenenergy of -2.90372 a.u. in comparison with the nonrelativistic limit, 2.903724377034119598296 a.u., obtained by Korobov using 2200 terms [*Phys Rev* **A 61** 064503 (2000)] The ground state energies of other systems obtained by the present study are also fairly accurate These simple correlated wavefunctions are expected to be highly useful for atomic scattering calculations

Keywords : Normal two-electron systems, Rayleigh-Ritz variational principle, Monte-Carlo optimization.

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The classical approach of including the effect of correlation in the study of two-electron systems is due to Hylleraas in the early thirties [1]. The first successful computation of the ground state energy was however performed by Pekeris [2] with an amazing accuracy of *eleven* significant digits with the inclusion of 1078 terms in the linear expansion of the wavefunction. Since then there have been several successful attempts to attain the essentially *exact* value for helium and other two-electron ionic species by different methods. In particular, mention may be made of the works of Freund *et al* [3], Drake and Yan [4], Umrigar *et al* [5], Frolov and Smith [6], and Korobov [7] who have maintained the highest order of accuracy in their calculations. There has however been continued interest in the study of the problem over the last seven decades in order to understand fully the intricate nature of the wavefunction in space and its dependence on the electron-electron correlation. Of late, search for a better understanding of the other physical parameters, such as, correlation and orbital cusps, virial theorem, various expectations, *etc* and their dependence on the two-electron wavefunction has also initiated many interesting studies [8–15].

In this Rapid Communication, we present a study to show the predominant dependence of the two-electron wavefunction on the exponential correlation. This work attempts to establish that proper inclusion of electron-electron correlation through exponential functions may be achieved when these are augmented with conventional terms containing higher powers of the electron and the relative coordinates with far less number of terms in the expansion. One of the main objectives of the present calculation has been to propose correlated wavefunctions for H^-, He and other two electrons systems which are fairly simple to be useful for atomic scattering calculations.

We have considered the two-electron wavefunction in the following forms :

I. $$\Psi = \varphi(r_1)\varphi(r_2)\chi(r_{12}) \qquad (1)$$

$$\frac{N}{\pi}\exp[-(Ar_1 + Br_2) + (1 \rightleftharpoons 2)] \times [1 + 0.5r_{12}\exp(-\mu r_{12})], \qquad (2)$$

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$$\text{II. } \Psi = \frac{N}{\pi}\exp\left[-(Ar_1 + Br_2) + (1 \rightleftarrows 2)\right] \times \left[1 + (0.5r_{12} + c_2 r_1 r_{12}^2)\exp(-\mu r_{12})\right], \quad (3)$$

$$\text{III. } \Psi = \frac{N}{\pi}\exp\left[-(Ar_1 + Br_2) + (1 \rightleftarrows 2)\right] \times \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 r_{12}^2 \exp(-\mu_2 r_{12})\right], \quad (4)$$

$$\text{IV. } \Psi = \frac{N}{\pi}\exp\left[-(Ar_1 + Br_2) + (1 \rightleftarrows 2)\right] \times \left[1 + (0.5r_{12} + c_2 r_1 r_2 r_{12}^2)\exp(-\mu r_{12})\right], \quad (5)$$

$$\text{V. } \Psi = \frac{N}{\pi}\exp\left[-(Ar_1 + Br_2) + (1 \rightleftarrows 2)\right] \times \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 r_2 r_{12}^2 \exp(-\mu_2 r_{12})\right], \quad (6)$$

$$\text{VI. } \Psi = \frac{N}{\pi}\exp\left[-(Ar_1 + Br_2) + (1 \rightleftarrows 2)\right] \times \left[1 + 0.5r_{12}\exp(-\mu_1 r_{12}) + c_2 r_1 \exp(-\mu_2 r_{12}) + c_3 r_2 \exp(-\mu_3 r_{12}) + c_4 r_1 r_{12}\exp(-\mu_4 r_{12}) + c_5 r_2 r_{12}\exp(-\mu_5 r_{12}) + c_6 r_1 r_2 \exp(-\mu_6 r_{12})\right]. \quad (7)$$

The seventh wavefunction considered in this series is of a general nature, and is obtained as

$$\text{VII. } \Psi = \frac{N}{\pi} e^{-A(r_1+r_2)}\left[c_0 + c_1 r_{12} e^{-\mu_1 r_{12}} + c_2 r_1 e^{-\mu_2 r_{12}} + c_3 r_1 r_2 e^{-\mu_3 r_{12}} + c_4 r_1 r_{12} e^{-\mu_4 r_{12}} + c_5 r_{12}^2 e^{-\mu_5 r_{12}} + c_6 r_1^2 e^{-\mu_6 r_{12}} + c_7 r_{12}^3 e^{-\mu_7 r_{12}} + c_8 r_1 r_2^2 e^{-\mu_8 r_{12}} + c_9 r_1 r_{12}^2 e^{-\mu_9 r_{12}} + c_{10} r_1^2 r_{12} e^{-\mu_{10} r_{12}} + c_{11} r_1 r_2 r_{12} e^{-\mu_{11} r_{12}} + c_{12} r_{12}^4 e^{-\mu_{12} r_{12}} + c_{13} r_1 r_2 r_1^2 r_{12} e^{-\mu_{13} r_{12}} + c_{14} r_1^2 r_2^2 e^{-\mu_{14} r_{12}} + c_{15} r_1 r_2^2 r_{12} e^{-\mu_{15} r_{12}} + c_{16} r_1 r_{12}^3 e^{-\mu_{16} r_{12}} + c_{17} r_1^2 r_2^2 r_{12} e^{-\mu_{17} r_{12}} + c_{18} r_1 r_2 r_{12}^3 e^{-\mu_{18} r_{12}} + c_{19} r_1 r_{12}^4 e^{-\mu_{19} r_{12}} + c_{20} r_1^2 r_2^2 r_{12}^2 e^{-\mu_{20} r_{12}} + c_{21} r_1 r_2 r_{12}^4 e^{-\mu_{21} r_{12}} + c_{22} r_1 r_2^2 r_{12}^3 e^{-\mu_{22} r_{12}} + c_{23} r_1 r_2^2 r_{12}^4 e^{-\mu_{23} r_{12}} + c_{24} r_1^2 r_2^2 r_{12}^3 e^{-\mu_{24} r_{12}} + (1 \rightleftarrows 2)\right]. \quad (8)$$

The recent studies of Toennis and coworkers [8], Le Sech [9], Bhattacharyya *et al* [10], Tripathi *et al* [11], Kar and Mandal [12] and Ghoshal *et al* [13] have considered different forms of the wavefunction for the two-electron systems with various degrees of sophistication. The eigenenergies predicted by these works are of interest since they all attempt to limit themselves to a small size of the basis set.

The standard eigenvalue problem to be solved, according to the Rayleigh-Ritz variational principle, is of the form : $\boldsymbol{Hc = \varepsilon Sc}$, where $\boldsymbol{H}$, $\boldsymbol{S}$ are respectively the hamiltonian and overlap matrices, with the vectors of expansion, $\boldsymbol{c}$ and eigenvalues, ε. In this calculation, there is a general prescription for evaluation of all the integrals analytically. We have reduced the given matrix eigenvalue equation to the standard form by multiplying both sides of the equation by $\boldsymbol{S}^{-1}$. The resulting eigenvalue equation is solved by transforming the matrix to the Hessenberg form and then using the Q-R algorithm following Press *et al* [14]. The vectors $\boldsymbol{c}$ are obtained by a further calculation by solving the linear equations.

As a further check of our calculations, we have also calculated the eigenvalues using the variational expression, $\varepsilon = \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$, which is an upper bound to the *exact* ground state energy of the system. The results seem to be very interesting.

We have displayed the main results of our findings in Tables 1 and 2 in which the eigenenergies are reported alongwith the expansion coefficients and exponential correlation μ_i as given by the wavefunctions I–VI for the two-electron systems, H , He, Li^+, C^{4+}, N^{5+}, Ne^{8+}. For the wavefunction VII, however, we display only the eigenenergies for these systems. (The results of the rest of the systems have been calculated and are with the authors which are available on request.) The best eigenenergy corresponding to the wavefunction VII for He is –2.90372 a.u. which seems to be a rather good estimate of the nonrelativistic value of –2.90372437703411959829 6 a.u., reported by Korobov [7] using 2200 terms (see also Pekeris [2], Freund *et al* [3], Drake and Yan [4]). A value of –2.90319 a.u. was reported by Roothaan and Weiss [15] using a 64-term open shell correlated wavefunction. The best values obtained by Kleinekathöfer *et al* [8] and Le Sech [9] for the same system are –2.90 a.u. and –2.9026 a.u. respectively. The eigenenergies of other systems are also in close agreement with the results of Pekeris [2].

One aspect that needs mentioning is that the relative values of the exponential correlation parameter for higher order terms in the expansion, increase with the charge of the nucleus, Z. Thus for $Z = 10$, the values of μ_i may at times become as large as 8.0 or 9.0 which may appear to be unacceptable. But we have tested our calculations by ignoring these terms. It is found that the results are then not so accurate as in the case when we retain these terms. Several significant digits are lost due to exclusion of these terms in the calculations.

Finally, a comment on our choice of the values of μ_i is in order. We have picked up random values of the exponential correlation parameter as well as of the effective charge, setting $A = B$. It is indeed an uphill task to optimise the set

Table 1. Eigenenergies in atomic units for the helium iso-electronic systems, H^-, He, Li^+, C^{4+}, N^{5+} and Ne^{8+} using exponential correlation functions I–V (see text)

		H^-	He	Li^+	C^{4+}	N^{5+}	Ne^{8+}
Wave I	$-\varepsilon$(a.u.)	0 525722	2.90110	7.27689	32 4027	44 7778	93 9031
	A	0.463	1.41	2.33	5 106	6 1091	8 944
	B	1.0712	2.2076	3.302	6 5233	7 5476	10 707
	μ	0 0536	0.1926	0.347	0 8603	0 9479	1 44
	N	0.256440	6 05268	26.6088	270 462	445 906	1376 13
Wave II	$-\varepsilon$(a.u.)	0.526160	2.90161	7.27789	32.4045	44 7798	93 9053
	A	0 5005	1 422	2.4075	5 2098	6 1598	9 0154
	B	1.0608	2 216	3.2821	6 4864	7 5412	10 6888
	μ	0.1219	0.2370	0.4321	1 1675	1 4434	2 3417
	c_2	0.0119	0 023	0.107	0 6522	1 018	2 7076
	N	0.278466	6.12797	27.2294	274.508	450 112	1387 72
Wave III	$-\varepsilon$(a u.)	0.526195	2.90185	7.27820	32 4044	44 7797	93 9052
	A	0.5214	1.4422	2.4069	5 2803	6.2244	9 0805
	B	1.0626	2.1943	3.2732	6 4397	7.4926	10 6332
	μ_1	0.1268	0 2636	0.5522	1 2319	1.4602	2 1754
	μ_2	0 1043	0 1414	0 3883	0 8486	0 9679	1.4518
	c_2	0.0136	0.0227	0.1343	0 612	0 8321	1.7494
	N	0.289996	6 19051	27 4002	276 796	452.278	1390.14
Wave IV	$-\varepsilon$(a.u.)	0.526543	2.90297	7.27906	32 4052	44.7804	93.9058
	A	0.4934	1.3940	2 304	5.0988	6.0298	8.8434
	B	1.1386	2 2750	3 3819	6.5972	7 6655	10.8494
	μ	0.0715	0.276	0.4693	1 0347	1.2548	1.9217
	c_2	0.003	0.036	0 1365	1 1045	1.8535	5.8822
	N	0 302331	6 30554	27.3246	274 437	449 576	1385 13
Wave V	$-\varepsilon$(a.u.)	0.526894	2.90315	7 27899	32.4046	44 7798	93 9020
	A	0.472	1.3940	2.315	5.1648	6 1075	9.063
	B	1.127	2 3000	3.36	6.5395	7.5937	10 686
	μ_1	0.077	0.2850	0.446	0.8922	1 0819	0.996
	μ_2	0.127	0.4600	0.433	0.5282	0 5426	0.293
	c_2	0.0032	0.074	0.114	0 5502	0 8118	0.754
	N	0.285282	6.37228	27.1637	274.595	449.759	1384.19

of nonlinear variational parameters μ_i apart from A. What we have achieved is definitely a solution to the eigenvalue problem satisfying the extremum principle for the eigenenergy. It may however, be possible to attain the same goal by optimising a different set of nonlinear variational parameters.

In conclusion, in this rapid communication, wavefunctions are proposed for the normal two-electron systems with predominant exponential correlation. These wavefunctions are fairly accurate in comparison to the *exact* wavefunctions. Because of their simple appearance and convenient structure, they are expected to be appropriate for atomic scattering theory.

All calculations were performed in Fortran 77 on IBM-compatible 750 MHz Pentium III PC with double precision arithmetic in the Linux environment.

Table 2. Eigenenergies in a.u. for the helium iso-electronic systems, H^-, He, Li^+, C^{4+}, N^{5+} and Ne^{8+} using exponential correlation functions VI and VII (see text).

		H^-	He	Li^+	C^{4+}	N^{5+}	Ne^{8+}
Wave VI	$-\varepsilon$(a.u.)	0.527100	2.90366	7.27970	32.4045	44.7806	93.9062
	A	0.418	1.4280	2.532	5.447	6.417	9.324
	B	1.109	2.3720	3.000	6.090	7.131	10.120
	μ_1	0.172	0.461	0.634	0.888	0.999	2.250
	μ_2	0.252	0.157	0.058	0.133	0.154	0.387
	μ_3	0.128	0.700	0.784	0.749	0.739	0.622
	μ_4	1.300	0.870	0.726	0.998	0.999	5.800
	μ_5	0.000	0.017	0.000	0.141	0.691	0.000
	μ_6	0.780	0.445	0.960	0.275	0.000	0.000
	c_2	−0.158	0 300	1.030	1.063	1.083	1.088
	c_3	−0.224	−0.306	−1.273	−1.262	−1.262	−1.377
	c_4	0.119	−0.356	−0.928	−0.999	−0.9999	−1.167
	c_5	0.0454	0.190	−0.0715	−0.108	−0.148	−0.001
	c_6	0.100	0.115	0.134	0.221	0.265	0.243
	N	0.315812	6.56939	27.7460	247.871	449.689	1391.90
Wave VII	$-\varepsilon$(a.u.)	0.527432	2.90372	7.27991	32.4062	44.7814	93.9068

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